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(71) Applicant: THE DOW CHEMICAL COMPANY
Dow Center 2030 Abbott Road Post Office Box 1967
Midland Michigan 48640(US)

(72) Inventor: Larsen, Eric Russell
314 W. Meadowbrook
Midland Michigan 48640(US)

(72) Inventor: Ecker, Ernest Levern
346 Dopp Road
Midland Michigan 48640(US)

(74) Representative: Smart, Peter John et al,
W.H. BECK, GREENER & CO 7 Stone Buildings Lincoln's Inn
London WC2A 3SZ(GB)

(54) Process for the production of 1,1,2-trichloro-2,2-difluoroethane.

(57) The compound 1,1,2-trichloro-2,2-difluoroethane is prepared in high yield by contacting 1,1-difluoroethylene and chlorine in the presence of a free radical initiator.

Croydon Printing Company Ltd.

PROCESS FOR THE PRODUCTION OF 1,1,2-TRICHLORO-2,2-DIFLUOROETHANE

This invention relates to a new method for the preparation of 1,1,2-trichloro-2,2-difluoroethane.

The compound 1,1,2-trichloro-2,2-difluoroethane has been prepared in the past by a variety of methods. These methods include the thermal chlorination of $CClF_2CH_3$ and CHF_2CH_3, the reduction of $CClF_2CCl_3$ with isopropanol (2-propanol), and the fluorination of CCl_3CHCl_2 with antimony fluoride. Except for the fluorination of CCl_3CHCl_2 and the reduction of $CClF_2CCl_3$, 1,1,2-trichloro-2,2-difluoroethane was not the major product and yields were generally poor. The fluorination of CCl_3CHCl_2 suffers as a method of preparing 1,1,2-trichloro-2,2-difluoroethane because it involves corrosive HF and produces a hazardous, antimony-containing waste stream. The reduction of $CClF_2CCl_3$ is not a satisfactory method of making 1,1,2-trichloro-2,2-difluoroethane, due to the fact that $CClF_2CCl_3$ is simply 1,1,2-trichloro-2,2-difluoroethane which has been overchlorinated.

In view of the deficiencies of the aforementioned known processes, it would be highly desirable to provide a process having a high selectivity to 1,1,2-trichloro-2,2-difluoroethane without having the problems associated with the methods of the prior art.

The present invention is such a highly selective process for producing 1,1,2-trichloro-2,2-difluoroethane. The process involves contacting 1,1-difluoroethylene with a chlorinating agent in the presence of a free radical initiator under conditions such that $CF_2ClCHCl_2$ is selectively obtained. Said selectivity is preferably greater than 63 mole percent based on 1,1-difluoroethylene. These selectivities are surprising in view of the results obtained by the techniques of the prior art.

The compound 1,1,2-trichloro-2,2-difluoroethane is a valuable intermediate for the preparation of highly desired chemicals. For example, 1,1,2-trichloro-2,2-difluoroethane may be combined with KOH and an alcohol to produce a halogenated ether via the method disclosed in British Patent Specification 523,449. Further, 1,1,2-trichloro-2,2-difluoroethane may be dehydrochlorinated to 1,1-dichloro-2,2-difluoroethylene, which in turn may be contacted with methanol in the presence of alkali to produce 2,2-dichloro-1,1-difluoroethyl methyl ether, as shown in U.S. Patent 3,264,356.

In the practice of the present invention it is essential to employ 1,1-difluoroethylene, a chlorinating agent, and a free radical initiator. The compound 1,1-difluoroethylene is well-known, is commercially available, and can be prepared by a number of known methods.

A suitable halogen or any agent that is capable of generating chlorin atoms, such as a suitable chlorine-containing solid or liquid, can be used as the chlorinating agent. The preferred chlorinating agent is chlorine. Advantageously, the chlorinating agent is supplied in an amount such that an optimum amount of 1,1,2-trichloro-2,2-difluoroethane is produced. Typically, the molar feed ratio of Cl_2 to 1,1-difluoroethylene is from 1.2 to 2.5, preferably this ratio is from 1.7 to 2.1. A lower or higher ratio may be employed, but low Cl_2/1,1-difluoroethylene molar feed ratios lead to excessive accumulation of CF_2ClCH_2Cl, while high ratios lead to accumulation of CF_2ClCCl_3 and a reduction in the selectivity of the process.

Suitable free radical initiators include catalysts, such as peroxides, and electromagnetic radiation. Electromagnetic radiation is the preferred free radical initiator. Any form of electromagnetic radiation which effects the instant chemical reaction may be employed, such as, for example, radiation in the visible and ultraviolet regions. Ultraviolet light is the most preferred free radical initiator. The output of the reaction system is a function of the light intensity, i.e., the rate of free radical formation, and the rate of addition of the reactants.

The chlorination of 1,1-difluoroethylene is advantageously conducted in a liquid reaction medium at a temperature which is between -20°C and 100°C. Preferably, the chlorination will be conducted between 0°C and 40°C. Ordinarily, the reaction will proceed readily at atmospheric or higher pressure; subatmospheric pressures can be employed if desired. Preferably, the chlorination is conducted at atmospheric pressure.

The reaction preferably takes place in the presence of a liquid reaction medium. The liquid reaction medium may be any suitable liquid which does not detract from the efficacy of the reaction. The liquid reaction medium preferably contains a molar excess of CF_2ClCH_2Cl with respect to $CF_2ClCHCl_2$, and the molar ratio of the former to the latter is typically 1.5 or greater. Preferably, the molar ratio of CF_2ClCH_2Cl to $CF_2ClCHCl_2$ in the liquid reaction medium will be from 2 to 10. Most preferably, this ratio will be from 3.5 to 10. A ratio of 1.5 will result in a selectivity to 1,1,2-trichloro-2,2-difluoroethane of approximately 63 percent. Ratios which are greater than 10 result in excessive recycle of CF_2ClCH_2Cl in exchange for a small small gain in selectivity. Preferably, a selectivity of 70 percent or more is obtained; most preferably a selectivity of 80 percent or greater is obtained. The term selectivity, when applied to the process of the present invention, means selectivity of 1,1,2-trichloro--2,2-difluoroethane, based on 1,1-difluoroethylene fed to the reaction vessel, and is calculated using the following equation:

$$\text{Selectivity} = (100)(Y)/(Y+Z) \; ;$$

wherein Y is moles of $CF_2ClCHCl_2$ in the product stream, and wherein Z is moles of CF_2ClCCl_3 in the product stream.

In a typical embodiment of the invention, the reaction vessel is charged with either CF_2ClCH_2Cl or a mixture, from a previous run, of CF_2ClCH_2Cl, $CF_2ClCHCl_2$, and CF_2ClCCl_3. The reaction vessel contents are irradiated by free-radical-initiating electromagnetic

radiation, and then gaseous chlorine and 1,1-difluoroethylene are fed simultaneously in separate feed streams having controlled flow rates to the reaction vessel through gas dispersion tubes. As the reaction proceeds, the liquid level rises in the reactor, gaseous HCl evolves from the liquid reaction medium, and the reactor is cooled in order to minimize vaporization of the relatively low boiling contents of the reactor (CF_2ClCH_2Cl boils at about 47°C), said vaporization being promoted by the heat of the exothermic reaction and the thermal energy given off by typical lamps used to generate free-radical-initiating electromagnetic radiation.

Prior to the point in time at which the reactor will overflow into its overflow line, which is connected to a reboiler of a distillation column, said reboiler is charged with CF_2ClCH_2Cl and heated to achieve a steady reflux. When the reactor overflows to the reboiler, the distillation column proceeds to separate the mixture in the reboiler. The temperature at the top of the distillation column is chosen so that the distillate is essentially pure CF_2ClCH_2Cl. A condenser at the top of the column condenses the vapors of the halogenated organic compounds. The condensate from the condenser is split into two streams; one for reflux to the distillation column and one as a recycle stream to the reactor.

The liquid in the reboiler becomes richer in 1,1,2-trichloro-2,2-difluoroethane and CF_2ClCCl_3 as the distillation progresses. This liquid may be withdrawn for purification, with a return of CF_2ClCH_2Cl to the reboiler. Alternatively, when the amount of 1,1,2-tri-

chloro-2,2-difluoroethane in the reboiler becomes sufficiently high, the chlorination may be halted and the distillation system can be used to purify the mixture. Then, after the purification is complete, the fraction rich in CF_2ClCH_2Cl can be returned to the reboiler, the chlorination may be restarted, and the cycle can be repeated as desired.

The following example is given to illustrate the invention and should not be construed as limiting its scope. All percentages in the example are by weight unless otherwise indicated.

Example 1

The process equipment includes:

(a) a 2.5 liter glass reaction vessel equipped with gas dispersion tubes at its lower end, a bottom drain, and a cooling means;

(b) a one-liter, 3-necked glass vessel (reboiler) equipped with a bottom drain, a thermocouple, and a heating means;

(c) a 1" x 18" glass distillation column packed with ¼" glass helices, and equipped with a thermocouple at its top and a vacuum jacket;

(d) a condensing means with an associated fraction-splitting means; and

(e) a 450 watt Hanovia® medium pressure, quartz, mercury vapor lamp.

The process equipment is assembled so that the packed distillation column sits above the one-liter vessel. The condensing means with associated fraction--splitting means sits above the distillation column.

The reaction vessel is placed so that any liquid overflow from it will flow by gravity to the one-liter vessel. Th source of electromagnetic radiation is placed so that it will irradiate the contents of the reaction vessel.

The process is initiated by charging the one-liter vessel with 3.83 moles of CF_2ClCH_2Cl and 0.13 moles of $CF_2ClCHCl_2$. The reaction vessel is charged with 20.5 moles of CF_2ClCH_2Cl, 3.41 moles of $CF_2ClCHCl_2$, and 0.35 moles of CF_2ClCCl_3. The one-liter vessel is heated so that a steady reflux is achieved through the distillation column. The lamp is placed approximately six inches (152 mm) away from the reaction vessel and is turned on.

At this point the gaseous reactants, chlorine and 1,1-difluoroethylene, are fed to the lower portion of the reaction vessel through the gas dispersion tubes. The molar feed ratio of Cl_2 to 1,1-difluoroethylene is 1.90. During a period of 29.35 hours 43.5 moles of Cl_2 and 22.9 moles of 1,1-difluoroethylene pass into the reaction vessel. During this same period, distillate from the one-liter vessel is passed into the reaction vessel at approximately 2.6 ml/min. The contents of the reaction vessel are clear, as opposed to being an undesirable yellow-green color which would indicate an excessive rate of chlorine addition.

The volume of liquid in the reaction vessel increases as the reaction progresses. The liquid overflows into the one-liter vessel through a line which contains a vapor seal. Gaseous HCl by-product is taken off the top of the reaction vessel and is routed to the

condensing means. The energy being supplied to the one-liter vessel via the heating means causes the overflow liquid to be distilled. A portion of the distillate is returned from the condensing means to the distillation column and the remaining portion is forwarded to the reaction vessel. The temperature at the top of the distillation column is controlled at 45-46°C in order to provide a distillate which is greater than 95 mole percent CF_2ClCH_2Cl. This allows the liquid in the one-liter vessel to become enriched in 1,1,2-trichloro--2,2-difluoroethane and CF_2ClCCl_3.

The one-liter vessel is partially emptied whenever it becomes nearly full and the removed mixture is partially separated into its components. The fraction rich in CF_2ClCH_2Cl is returned to the one-liter vessel. For the total period of the run, 5.30 moles of CF_2ClCH_2Cl and 0.25 moles of $CF_2ClCHCl_2$ are returned to the one-liter vessel.

The total weight of all materials added to the system is 9.260 kg, of which 9.147 kg remain at the end of the run. The molar amounts, according to gas-liquid chromatographic analysis, of materials added to the system and recovered therefrom for the run are shown in Table I.

TABLE I

Mass Balance

Component	Moles In	Moles Out
$CF_2=CH_2$	22.9	-
Cl_2	43.49	-
CF_2ClCCl_3	0.35	2.35
$CF_2ClCHCl_2$	3.8	17.6
CF_2ClCH_2Cl	29.6	35.5
HCl	-	20.5
Total Organic	56.65	55.45

Organic recovery = 98 mole percent.

Calculated Yield of 1,1,2-trichloro-2,2-difluoroethane = 82.8 mole percent based on $CF_2=CH_2$ fed.

Selectivity = 87.3 mole percent.

Conversion of $CF_2=CH_2$ = 100 percent.

CLAIMS

1. A process for the production of 1,1,2-trichloro-2,2-difluoroethane comprising contacting 1,1-difluoroethylene with a chlorinating agent in the presence of a free radical initiator under conditions such that 1,1,2-trichloro-2,2-difluoroethane is obtained.

2. A process as claimed in Claim 1 wherein the chlorinating agent is chlorine.

3. A process as claimed in Claim 1 or Claim 2 wherein the free radical initiator is electromagnetic radiation.

4. A process as claimed in any preceding claim wherein the chlorinating agent and 1,1-difluoroethylene are contacted in a liquid reaction medium.

5. A process as claimed in any preceding claim wherein the temperature of the liquid reaction medium is between -20°C and 100°C.

6. A process as claimed in Claim 4 wherein the liquid reaction medium comprises CF_2ClCH_2Cl and $CF_2ClCHCl_2$ in a molar ratio which is at least 1.5 of the former to 1 of the latter, and wherein the molar feed ratio of the chlorinating agent expressed as available chlorine to 1,1-difluoroethylene is from 1.2 to 2.5.

7. A process as claimed in any one of Claims 4 to 6 wherein the molar feed ratio of the chlorinating agent

expressed as available chlorine to 1,1-difluoroethylene is from 1.7 to 2.1, the temperature of the liquid reaction medium is from 0°C to 40°C, the liquid reaction medium comprises CF_2ClCH_2Cl and $CF_2ClCHCl_2$ in a molar ratio of from 2 to 10, and the free radical initiator is ultraviolet light.

8. A process for the production of 1,1,2-trichloro-2,2-difluoroethane comprising contacting 1,1-difluoroethylene with chlorine in the presence of ultraviolet light at a temperature of from about -20°C to about 100°C in a liquid reaction medium comprising CF_2ClCH_2Cl and $CF_2ClCHCl_2$ wherein the molar ratio of CF_2ClCH_2Cl to $CF_2ClCHCl_2$ is at least about 1.5:1, thereby selectively producing 1,1,2-trichloro-2,2-difluoroethane.

9. A process as claimed in any one of Claims 1 to 8 wherein a portion of the liquid reaction medium is removed continuously or intermittently during the course of the reaction and a fraction rich in 1,1,2-trichloro-2,2-difluoroethane and a fraction rich in CF_2ClCH_2Cl are obtained therefrom and wherein the fraction rich in CF_2ClCH_2Cl is recycled to the liquid reaction medium.

10. A process as claimed in any preceding claim wherein the 1,1,2-trichloro-2,2-difluoroethane is obtained with a selectivity of greater than 63 mole percent.

11. A process as claimed in Claim 10 wherein th selectivity is at least 80 mole percent.

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EUROPEAN SEARCH REPORT

0143864
Application number

EP 83 30 7328

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
	No relevant documents have been disclosed. -----		C 07 C 19/08 C 07 C 17/06
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 07 C 19/00 C 07 C 17/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	06-07-1984	VAN GEYT J.J.A.

CATEGORY OF CITED DOCUMENTS

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